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㉚ Surface treating method for polyacetal resin molded articles.

㉛ A surface treating method for polyacetal resin molded articles is characterized in that the surface of a molded article made of a polyacetal resin composition comprising 99.5 - 80 parts by weight of a polyacetal resin and 0.5 - 20 parts by weight of one or more kinds of fine powdery metallic oxides having a mean particle diameter of 0.1 - 20 μ is etched with an acidic solution containing one or more kinds of inorganic acids selected from the group consisting of sulfuric acid, hydrochloric acid, and phosphoric acid.

Surface Treating Method for Polyacetal Resin Molded Articles

[Industrial Field of Application]

This invention relates to a surface treating method for polyacetal resin molded articles. More particularly, the invention relates to a surface treating method for efficiently obtaining polyacetal resin molded articles having surface characteristics suitable for surface decoration by printing, coating, deposition, plating, and otherwise, and/or for adhesion with an adhesive.

10 [Prior Art]

Polyacetal resins are chemically very stable and lacking in surface activity. This, coupled with the fact that there is no suitable solvent available which has good affinity to such resin, has virtually defied the possibility of subjecting products of such resin to such surface decoration as plating, printing, coating, or deposition, or surface bonding with an adhesive. Therefore, such resin has practically been not used for uses requiring such finished. Recently, however, uses of polyacetal resins have tended to become diversified and sophisticated, and therefore the current trend is such that for some uses such special characteristics as decorativeness adhesion properties are sometimes required in addition to good mechanical, physical, and chemical properties and functional features. More particularly, for applications such as exterior trim parts, metallic surface characteristics are often required.

As attempts to improve the surface workability of polyacetal resins, for example, their adaptability to surface cladding, methods for treating the surface of a molded article with phosphoric acid, p-toluenesulfonic acid, sulfuric acid, etc. have been proposed in the specifications of U.S. Pat. No. 3,235,426, U.S. Pat. No. 3,554,880, U.S. Pat. No. 3,905,887, and U.S. Pat. No. 3,963,590. With these methods, however, it is difficult to impart such surface workability to polyacetal resin molded articles as will meet practical utility requirements.

As more recent approaches for surface treatment of polyacetal resins, Japanese Provisional Patent Publication Nos. 78023 Of 1980 and 152845 of 1981 disclose methods of the kind that a polyacetal resin is mixed with a material, such as metallic carbonate which can easily be eluted with acid and that after molding, the metallic salt is eluted with a specific acid for removal, whereby the surface of the molded article is roughened. These methods mark a large step toward practicability of surface treatment, and actually they are in use for some applications. However, these methods involve difficulties in that, under the action of the carbonate or the like, not only is the material liable to discoloration and loss of property stability due to thermal history in the course of composition preparation and molding operation, but also the surface working characteristics of the molded article are likely to vary.

Summary of the Invention

In order to overcome these difficulties and obtain a polyacetal molded article having good surface working characteristics, the present inventors made extensive studies on resin compositions and surface treatment and as a result they found that if the surface of a molded article made of a polyacetal resin composition comprising 99.5 ~ 80 parts by weight of a polyacetal resin and 0.5 ~ 20 parts by weight of one or more kinds of fine powdery metallic oxides having a mean particle diameter of 0.1 ~ 20 μ was etched with an acidic solution containing one or more kinds of inorganic acids selected from the group consisting of sulfuric acid, hydrochloric acid, and phosphoric acid, the surface working characteristics of the polyacetal resin molded article could be improved. This finding led to the present invention.

In other words, the invention provides a method for treating a moulded article of polyacetal on its surface, which comprises the step of etching an article moulded from a polyacetal composition comprising 80 to 99.5 parts by weight of a polyacetal resin and 20 to 0.5 parts by weight of fine particles of a metal oxide having an average particle diameter of 0.1 to 20 microns with an acidic solution containing an inorganic acid selected from the group consisting of sulfuric acid, hydrochloric acid and phosphoric acid.

It is preferable that the metal oxide is an oxide of a metal belonging to the group II of the periodic table and the acidic solution contains both sulfuric acid and hydrochloric acid or both sulfuric acid and phosphoric acids.

In the invention, the term "metallic oxides" refers to compounds such as, for example, magnesium oxide, calcium oxide, barium oxide, zinc oxide, aluminum oxide, and titanium oxide, and one or more of these kinds of oxides are used; more particularly, oxides of group II metals in the periodic table are preferred.

5 The reason why the use of such fine powdery metallic oxide is effective for the purpose of the invention is presumably that whereas if no such filler is used, a chemically stable non-crystalline skin layer is formed on the surface of the crystalline polyacetal resin molded article, which hinders the formation of a roughened surface, the fine powdery metallic oxide, if incorporated by admixture with the resin, acts as a nucleating agent to develop crystallization to the surface layer, thereby facilitating surface erosion, and the metallic
10 oxide elutes itself to help in effective etching.

In the invention, such metallic oxide in fine powder form having a mean particle diameter of $0.1 \sim 20\mu$ is used. If the mean particle diameter is less than 0.1μ , no sufficient effect of surface roughening is obtainable by the process of acid treatment which will be described hereinafter, it being thus unable to obtain a molded article having good surface working characteristics. If the mean particle diameter is more
15 than 20μ , the surface will be excessively roughened, it being thus unable to obtain good mirror finish or sufficient adhesion in the process of after-treatment, such as plating, for example. Preferably, such metallic oxide having a mean particle diameter of $0.3 \sim 10\mu$, more preferably $0.5 \sim 5\mu$, is used.

If the proportion of such metallic oxide is too small, no sufficient surface roughening can be effected by acid treatment, and thus good surface workability, e.g. a strong plating bond, cannot be obtained. If the
20 proportion is too large, the resin will be degraded in mechanical strength, moldability, and the like characteristics, and further the extent of surface roughening will be excessive, thus leading to poor appearance. Considering the balance of these, the ratio of polyacetal resin/metallic oxide is $99.5 \sim 8\mu/0.5 \sim 2\mu$ by weight, preferably $99 \sim 90/1 \sim 10$.

Polyacetal resins useful for the purpose of the invention are not particularly limited. Polyacetal
25 homopolymers and polyacetal copolymers in which a larger part of a main chain consists of an oxymethylene chain, and also modified forms of these polyacetal resins which are obtained by known crosslinking or graft copolymerization techniques, may be equally effectively used as base resins for the purpose of the invention.

It is desirable to incorporate such known additives as an anti-oxidant and a heat stabilizer by admixture
30 into a polyacetal resin composition used in the invention. Further, depending upon the purpose for which the product is used, it is possible to incorporate by admixture any known material which is usually added to any ordinary type of thermoplastic or thermosetting resin, insofar as it is not much detrimental to the process of surface roughening with an etching solution and to the post-etching surface working characteristics and other properties of the molded article.

35 For example, various kinds of stabilizers for light resisting and weathering purposes, lubricants, parting agents, plasticizers, nucleating agents, antistatic agents, surface active agents, and lubricating agents may be used for such addition.

The polyacetal resin used as a base may be mixed with any of other kinds of thermoplastic resins including, for example, polyurethane resin, fluorine plastic, polyethylene, polypropylene; olefin monopolymer
40 or copolymer, such as ethylene-propylene copolymer, ethylene-vinyl acetate copolymer, or ethylene-alkylacrylate copolymer; vinyl-based compound, such as styrene-butadiene-acrylonitrile copolymer or styrene-acrylonitrile copolymer, and their copolymers; graft copolymer composed of polyacrylate resins; polyamide resins; polymers of thermoplastic segment type copolyesters; and other organic polymeric materials including modified forms of these resins. Further, a molded article made of such composition may
45 incorporate any of such materials as glass fiber, metallic fiber, boron, potassium titanate, ceramic, glass flake, glass bead, mica, talc, highly dispersible silicate, silica flour, quartz sand, wollastonite, various kinds of metallic powder, metallic foil, and other inorganic compounds in fibrous, lamellar, granular, and powdery forms, & such as silicon carbide, boron nitride, and silicon nitride, also their whiskers and metallic whiskers.

Molded articles made of such composition according to the invention can be easily produced by any
50 known method. For example, one method is such that after individual ingredients are mixed together, the mixture is kneaded and extruded by an extruder into a pellet, the pellet being then molded to shape. Another method is such that pellets of different compositions are first prepared and then they are mixed in predetermined proportions, the mixture being subjected to molding, so that a mold article of a predetermined composition is obtained after molding operation. Another available method is such that individual
55 ingredients are directly supplied into a molding machine. Any of these methods can be conveniently employed.

According to the invention, such polyacetal resin molded article is subjected to etching, for which purpose an acidic solution containing one or more kinds of inorganic acids selected from the group

consisting of sulfuric acid, hydrochloric acid, and phosphoric acid is used. Treatment with an acidic solution containing none of these acids cannot provide any sufficient surface working characteristics. Use of a treating solution containing an oxidative acid in any excessive proportion is undesirable, because it will invite excessive surface roughening, thus causing strength reduction and poor mirror effect. According to the invention, an aqueous mixture solution of sulfuric acid and hydrochloric acid and an aqueous mixture solution of sulfuric acid and phosphoric acid are advantageously used; and preferred mixture ratios in these aqueous solutions are: 96% sulfuric acid /36% hydrochloric acid/water = 20 - 60/5 - 30/the rest (in wt %); and 96% sulfuric acid /85% phosphoric acid /water = 20 - 60/20 - 60 /the rest (in wt %).

For the purpose of etching the polyacetal molded article with such acidic solution, optimum dipping conditions are suitably pursued and selected according to the composition of the etching solution, but generally preferred conditions are 5 sec - 30 min dipping at 10 - 80 °C. Optimum conditions are often selected within this range.

Such etching solution according to the invention may incorporate by admixture any of such materials as thioureas, amines, amides, or thioethers in order to prevent poor roughening due to deterioration of the solution with time, or a surface active agent in order to prevent bubble deposition on the surface of the molded article in the process of etching.

In the invention, it is also possible to subject the molded article to a known treatment prior to or after or simultaneously with etching. For example, the molded article may be heat treated or hot-water treated, or dipped in a solution containing a particular compound before or after etching. Such treatment after etching may be carried out in combination with stages for neutralization of the etching solution, washing, drying, etc.

[Examples]

The treating method of the invention will be described in further detail with reference to the following examples and comparative examples. It is to be understood, however, that the invention is not limited by these examples.

Examples 1 - 7 and Comparative Example 1

Ninety-five parts by weight of a polyacetal resin, "Jurakon® M90" (an acetal copolymer, ordinary grade, produced by Polyplastics Co.) and 5 parts by weight of each one of the metallic oxides shown in Table 1 were premixed in a tumbler, and the mixture was then melt kneaded in an extruder, being extruded therefrom in the form of a pellet. Test specimens (each of 70 mm x 50 mm x 3 mm) were prepared by employing an injection molding machine.

Each test specimen was dipped and washed in a commercially available alkaline degreaser "Ace Kurin A220" (producer by Okuno Seiyaku Kogyo K.K.) at 80 °C for 5 min, and then it was dipped for etching in a solution composed of 96% sulfuric acid /85% phosphoric acid /water = 40 /25 / 35 (weight ratio) at 40 °C for 8 min.

After etching, the specimen was washed in water and then dipped in a 5 wt % sodium hydroxide solution for 3 min. for neutralization.

After being neutralized, the specimen was water-washed and then dipped in a commercially available catalyzing solution "Catalyst" (produced by Okuno Seiyaku Kogyo K.K.) for 3 min. After water-washing, the specimen was dipped in a 5 wt % hydrochloric acid solution for 2 min, being thereby surface-activated. After surface activation, it was dipped in a commercially available electroless nickel solution (produced by Okuno Seiyaku Kogyo K.K., TMP nickel plating solution) for 12 min treatment at 35 °C. The process of pre-treatment was thus completed.

After the pre-treatment, the specimen was subjected to electroplating in a predetermined manner. A mean deposit thickness was set at: copper 40 μm, nickel 10 μm, and chrome 0.1 μm. Performance characteristics of the specimens thus plated were as shown in Table 1.

Plate peel strength was determined in the following manner: 10 mm wide parallel cuts were made on the plate surface and one end of such cut was lifted and pulled in a direction angled at 90° to the surface of the test specimen, the stress of the pull being taken as plate peel strength. Appearance evaluation was made by visual inspection through naked eye. The degree of adhesivity required for practical service is considered to be 1 kg/cm or more, and in the light of this criterion, the resin molded article specimens which were surface treated according to the method of the invention were found as being well qualified for

practical use.

For the purpose of comparison, specimens incorporating no metallic oxide were plated according to same recipes as used in Examples 1 ~ 7, but no plate with good adhesion effect was obtained. The results are also shown in Table.

Table 1

	Filler			*1 Appear- ance	Plate peel strength (kg / cm)
	Kind	Mean pcle dia (μ m)	Propn (wt part)		
Example 1	Calcium oxide (CaO)	4.0	5.0	○	2.3
Example 2	Barium oxide (BaO)	5.0	5.0	○	2.1
Example 3	Magnesium oxide (MgO)	5.0	5.0	○	2.5
Example 4	Zinc oxide (ZnO)	0.5	5.0	○	2.4
Example 5	Titanium oxide (TiO ₂)	0.5	5.0	○	1.7
Example 6	Aluminum oxide (Al ₂ O ₃)	0.5	5.0	○	1.6
Example 7	Boron oxide (B ₂ O ₃)	3.5	5.0	○	1.4
Comp. Ex 1	-			⊙	0.5

*1 Visually evaluated.

⊙ Highly specular

○ Generally specular (reflected image not dim)

△ Reflected image slightly dim

× Specular effect poor (image dim).

Examples 8 - 9 and Comparative Examples 2 - 3

Specimens incorporating the same magnesium oxide having a mean particle diameter of 5μ) as in Example 3 were treated and plated in same way as in Example 3, except that the proportion of the magnesium oxide was varied from that in Example 3.

The results are shown in Table 2.

Table 2

	poly-acetal resin / mag- nesium oxide (wt part)	*1 Plate appear.	Plate peel str. (kg/cm)	Before-plating	
				tensile str. (kg/cm ²)	stretch (%)
(Comp. Exp. 1)	100/0	⊙	0.5	620	24
Comp. Exp. 2	99.75/0.25	⊙	0.7	620	21
Example 8	98/2	○	1.8	610	20
(Example 3)	95/5	○	2.5	590	16
Example 9	90/10	○	2.3	550	12
Comp. Exp. 3	70/30	×	1.4	430	5

*1 See Table 1.

Examples 10 - 12, and Comparative Example 4

In each case, 95 parts by weight of aforesaid polyacetal resin were mixed with 5 parts by weight of a magnesium oxide having such mean particle diameter as shown. Specimens were treated and plated in same manner as in Example 3.

The results are shown in Table 3.

Table 3

	Magnesium oxide		*1 Plate appear.	Plate peel str. (kg/cm)
	Mean particle dia (μm)	Propn (wt pt)		
Example 10	0.3	5	○	1.9
Example 11	1.5	5	○	2.4
(Exp. 3)	5.0	5	○	2.5
Example 12	12.0	5	○ *2	2.0
Comp. Exp 4	30.0	5	△ *3	1.5

*1 See Table 1.

*2 Microspots were present on the surface.

*3 Relatively large spots were present in large number on the surface; not qualified for practical use.

Examples 13 - 17 and Comparative Examples 5 - 6

Same experiments as Example 3 were carried out except that the composition of etching solution was varied. Etching solution compositions used and evaluation results are shown in Table 4. For the purpose of comparison, evaluation was likewise made with respect to other etching solutions in which an acid other than those specified in the invention was used.

The results are shown in Table 4.

Table 4

	Etching solution composition (wt part)	Etching time	Plate *1 appearance	Plate peel strength (kg/cm)
(Example 3)	96% sulfuric acid/85% phosphoric acid/water = 40/25/35	40 °C x 8 min	○	2.5
Example 13	" = 28/42/30	40 °C x 10 min	○	2.1
Example 14	" = 55/10/35	40 °C x 5 min	○	2.4
Example 15	96% sulfuric acid/36% hydrochloric acid/water = 35/20/45	25 °C x 15 min	○	2.4
Example 16	" = 48/12/40	25 °C x 15 min	○	2.3
Example 17	" = 45/0/55	40 °C x 10 min	○	1.5
Comp. Ex 5	98% nitric acid/water = 60/40	40°C x 10 min	△	0.8
Comp. Ex 6	90% formic acid = 100	40°C x 30 min	○	0.6

* See Table 1.

Example 18 and Comparative Example 7

Treatment and evaluation were made in same manner as in Example 3, except that an acetal homopolymer "Tenac® 5010" (produced by Asahi Chemical Industry Co.) was used in place of the Example 3 polyacetal resin. For the purpose of comparison, specimens containing no magnesium oxide were also evaluated in same manner.

The results are shown in Table 5.

Table 5

	Filler			*1 Plat appear.	Plate peet str. (kg/cm)
	Kind	Mean pcle dia (μ m)	Propn (wt part)		
Example 18	Magnesium oxide	5	5	○	2.1
Comp. Exp 7	-	-	-	⊙	0.6

*1 See Table 1.

Examples 19 - 21 and Comparative Examples 8 - 10

A resin composition comprising 95 parts by weight of a polyacetal resin "Jurakon® M90" (produced by Polyplastics Co., Ltd.) and 5 parts by weight of magnesium oxide was used. After having been detained for 2 - 30 min in an injection molding machine set at a cylinder temperature of 200 °C (except for the feeder portion which was set at 170 °C), the composition was molded into test specimens. Etching was then carried out in same manner as in Examples 1 - 7. Plating was effected, and evaluation was made as to those items shown in Table 6.

For the purpose of comparison, specimens prepared from a composition containing calcium carbonate instead of magnesium oxide were used and evaluation was made in same manner.

Results are shown in Table 6.

With those incorporating calcium carbonate, it was observed that with the increase in the time of detention in the molding machine, the plate adhesivity was somewhat lowered and the performance characteristics varied widely. Apparently, they showed lack of stability. In contrast, no problem was seen with the specimens containing magnesium oxide in accordance with the invention.

Table 6

	Filler			Molder detention time (min)	*2 Molding discolor- ation	*1 Plate appear- ance	Plate peel test (n=10)		
	Kind	Mean particle dia (μm)	Propn. (wt part)				Peel str (kg/cm)	Varia- bility R (kg/cm)	σ (kg/cm)
Example 19	Magnesium oxide (MgO)	5.0	5	2	⊙	○	2.5	0.5	0.15
Example 20	"	5.0	5	10	○	○	2.4	0.4	0.15
Example 21	"	5.0	5	30	○~△	○	2.5	0.6	0.18
Comp. Ex 8	Calcium car- bonate (CaCO ₃)	5.0	5	2	⊙	○	2.3	0.6	0.18
Comp. Ex 9	"	5.0	5	10	△	○	2.0	0.9	0.24
Comp. Ex 10	"	5.0	5	30	⊗	○~△	1.9	1.4	0.31

*1 See Table 1.

*2 Degree of yellowing

⊙ ← No yellowing → ⊗ Yellowing noticeable
 ⊙ ⊗

[Advantage of the Invention]

5 As is clear from the foregoing description and above given examples, by surface treating a molded article made from a composition comprising a polyacetal resin and, in mixture therewith, a metallic oxide having a mean particle diameter of $0.1 \sim 20\mu$ with an acidic solution containing one or more kinds of inorganic acids selected from the group consisting of sulfuric acid, hydrochloric acid, and phosphoric acid,
 10 it is now possible to notably improve the surface working characteristics of the molded article, such as, for example, surface affinity to plating and coating, without detriment to the inherent excellent properties of polyacetal resins.

15 Claims

- 1-A method for treating a moulded article of polyacetal on its surface, which comprises the step of etching an article moulded from a polyacetal composition comprising 80 to 99.5 parts by weight of a polyacetal resin and 20 to 0.5 parts by weight of fine particles of a metal oxide having an average particle
 20 diameter of 0.1 to 20 microns with an acidic solution containing an inorganic acid selected from the group consisting of sulfuric acid, hydrochloric acid and phosphoric acid.
- 2-A method as claimed in Claim 1, in which the metal oxide is an oxide of a metal belonging to the group II of the periodic table.
- 3. A method as claimed in Claim 1 or Claim 2, in which said acidic solution contains both sulfuric acid
 25 and hydrochloric acid or both sulfuric acid and Phosphoric acid.
- 4. A method as claimed in any preceding claim, in which the metal oxide has an average particle diameter of 0.5 ~ 5 microns.
- 5. A method as claimed in any preceding claim in which the ratio of polyacetal resin to metallic oxide is 99 ~ 90 to 1 ~ 10 by weight.
- 30 6. A method as claimed in any preceding claim, in which the polyacetal resin includes an anti-oxidant and a heat stabiliser.
- 7. A method as claimed in any preceding claim, in which the acidic solution contains 20 ~ 60% by weight of sulphuric acid (measured as 96% acid) and either 5 ~ 30% by weight of hydrochloric acids (measured as 36% acid) or 20 ~ 60% phosphoric acids (measured as 85% acid).
- 35 8. A method as claimed in any preceding claim, in which the treatment is conducted by dipping the moulded article in the acidic solution for a period of 5 sec ~ 30 min at $10 \sim 80^{\circ}\text{C}$.
- 9. A moulded article of polyacetal whenever prepared by a process as claimed in any preceding claim.

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EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
E	EP-A-0 259 011 (POLYPLASTICS CO. LTD) * Claims 1-5; page 3, lines 5,6,27-40,54; examples * -----	1-9	C 08 J 7/14
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
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The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 22-09-1989	Examiner HALLEMEESCH A.D.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document I : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document			